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Development and Demonstration of Insulated Pressure Vessels for Vehicular Hydrogen Storage

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Development and Demonstration of Insulated Pressure Vessels for Vehicular Hydrogen Storage

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Abstract
This paper describes the development of an alternative technology for vehicular storage of hydrogen. Insulated pressure vessels are cryogenic-capable pressure vessels that can accept cryogenic liquid fuel, cryogenic compressed gas or compressed gas at ambient temperature. Insulated pressure vessels offer advantages over alternative hydrogen storage technologies. Insulated pressure vessels are more compact and less expensive than compressed hydrogen vessels. They have lower evaporative losses and lower energy requirement for fuel liquefaction than liquid hydrogen tanks, and they are lighter than hydrides.
The work described in this paper is directed at verifying that insulated pressure vessels can be used safely for vehicular hydrogen storage. The paper describes multiple tests and analyses that have been conducted to evaluate the safety of insulated pressure vessels. Insulated pressure vessels have been subjected to multiple DOT, ISO and SAE certification tests, and the vessels have always been successful in meeting the passing criteria for the different tests. A draft procedure for insulated pressure vessel certification has been generated to assist in a future commercialization of this technology. Ongoing work includes the demonstration of this technology in a vehicle.

Keywords: hydrogen storage, cryogenic hydrogen, pressure vessels

1. Introduction

Hydrogen-fueled vehicles have many features that make them serious candidates as alternatives to today's petroleum-powered vehicles. Hydrogen vehicles can use advanced technologies to greatly improve environmental quality and reduce to practically zero automotive emissions of regulated pollutants. Greenhouse gas emissions can also be reduced if hydrogen is obtained from renewable or nuclear sources, leading to a carbon-free system. At the same time, hydrogen vehicles have the capability of providing the range, performance, and utility of today's gasoline vehicles.
A fundamental problem with hydrogen vehicles is storing enough hydrogen on board. Hydrogen is the lightest of all the fuels, but it is also the least compact (Figure 1), due chiefly to the simplicity of the H_2 molecule. Unlike polyatomic hydrocarbon fuels such as gasoline (C_8H_{18}), H_2 consists of just two monovalent atoms. This unique structure gives H_2 extreme combustion characteristics (e.g. low ignition energy, low emissivity, wide flammability limits, high flame speed) and physical properties (high diffusivity, thermal conductivity, buoyancy, and incompressibility). An extremely low boiling point (20.3 K), second only to helium, gives LH_2 a very large coefficient of thermal expansion, expanding nearly 40% between 20 K and 30 K.
Particularly striking is the very low atomic density of H_2 both as a compressed gas and as a cryogenic liquid. There are fewer hydrogen atoms by volume in LH_2 than in metal hydrides, most fuels, and common molecular liquids such as octane (C_8H_{18}), ethanol (CH_3CH_2OH),

methanol (CH_3OH), cryogenic liquid methane (LCH_4), ammonia (NH_3), hydrazine (N_2H_4), hydrogen peroxide (H_2O_2), and even H_2O (Figure 2).

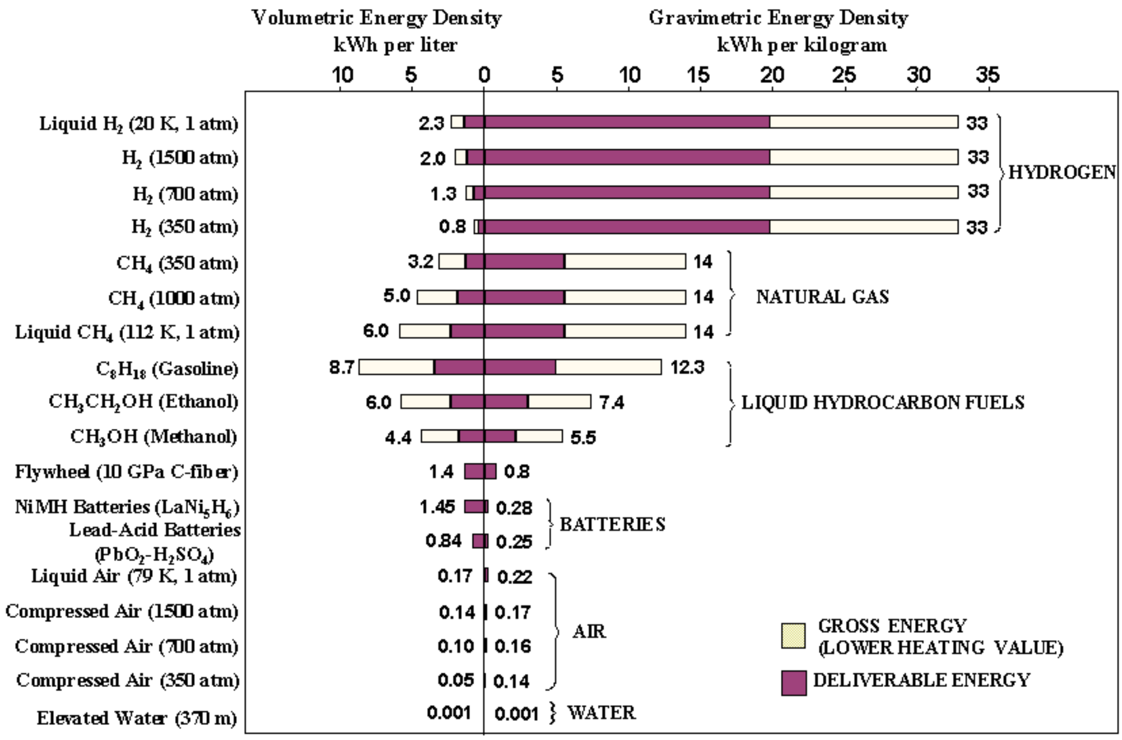

Figure 1. Theoretical intrinsic gravimetric and volumetric energy densities of fuels (on an LHV basis) and energy storage technologies. Compressed air and gaseous fuels are shown at 300 K and various pressures, liquids are shown at 300 K or (if cryogenic) their boiling point. The mass and volume of containment vessels is excluded. Energy densities for flywheels and batteries include only active mass. The values given for compressed air represent maximum possible system work. Numerical values indicate gross energy densities. Maximum *deliverable* energy densities are graphically indicated for assumed efficiencies of 100% for all energy storage systems, 60% for hydrogen powered fuel cells, and 40% for hydrocarbon fuels used in automotive scale combustion engines.

There are at least three viable technologies for storing hydrogen fuel in cars. They are compressed hydrogen gas (CH_2), metal hydride adsorption, and cryogenic liquid hydrogen (LH_2). Each of these has significant disadvantages. Storage of CH_2 requires a big volume that is difficult to package in vehicles. Tanks for CH_2 storage are likely to be expensive. Hydrides are extremely heavy, resulting in a substantial reduction in vehicle fuel economy and performance. Low-pressure LH_2 storage is light and compact, and has received significant attention due to its packaging advantages. Disadvantages of low-pressure LH_2 storage are the substantial amount of electricity required for liquefying the hydrogen (40% of the lower heating value); the evaporation losses that may occur during fueling low-pressure LH_2 tanks; and the evaporation losses that occur during periods of inactivity, due to heat transfer from the environment.

The proposed alternative to vehicular hydrogen storage consists of storing fuel in an insulated pressure vessel that has the capability to operate at cryogenic temperature (20 K), and at high pressure (25 MPa or higher). This vessel has the flexibility of accepting cryogenic liquid, cryogenic compressed gas or ambient temperature compressed gas as a fuel.

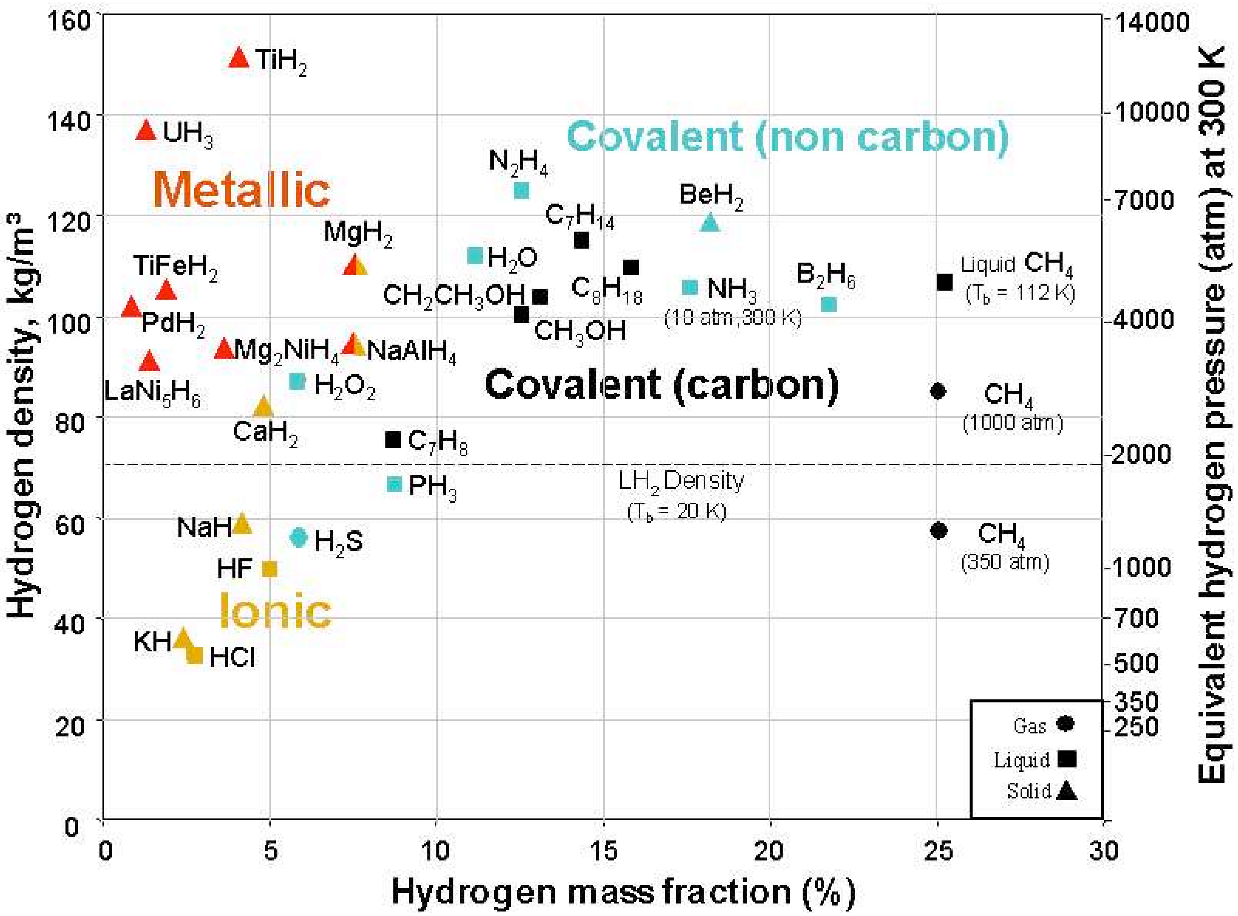

Figure 2. Density and mass fraction of hydrogen contained in substances spanning a spectrum of ionic, covalent, and metallic (both high temperature and low temperature) hydrides. Hydrocarbon fuels are also shown, including compressed methane (CH_4) at 300 K. The right hand scale (non linear) shows the pressure needed to achieve an equivalent density of compressed hydrogen gas at 300 K. The dashed line indicates that the density (70 kg/m^3) of liquid hydrogen (LH_2) at its boiling point (20 K) is substantially lower than the atomic hydrogen density of many compounds.

The fueling flexibility of the insulated pressure vessels results in significant advantages. Fuel energy requirements are lower than for conventional low-pressure cryogenic fuel tanks because a car with an insulated pressure vessel can use, but does not require, a cryogenic fuel. A hybrid or fuel cell vehicle with a gasoline-equivalent fuel consumption of 2.94 l/100 km could be refueled with ambient-temperature compressed hydrogen at 25 MPa and still achieve a 200 km range, suitable for most trips. The liquid cryogenic fuel would only be considered for long trips, the additional range resulting in additional cost to the user. It is anticipated that vehicles equipped with an insulated pressure vessel would refuel most of the time with ambient-temperature compressed fuel. The user would consume less energy, benefit from a lower fuel cost and yet still have 3 times the potential range of conventional ambient-temperature storage systems. In addition, use of compressed hydrogen for all trips under 240 km, (which represent 85% of all the distance traveled in the USA) would reduce the total energy consumption of the vehicle by 16% compared to a vehicle filled with LH_2.
In addition to this, insulated pressure vessels have substantially reduced evaporative losses compared to liquid hydrogen tanks. Evaporative losses are lower both in the case that a

vehicle is parked for a long period of time, and in the case in which the vehicle is driven a short distance every day. See [1] for a detailed thermodynamic analysis of this process.
From engineering and economic perspectives, insulated pressure vessels strike a versatile balance between the cost and bulk of ambient temperature compressed fuel storage, and the energy efficiency, thermal insulation and evaporative losses of cryogenic storage. Insulated pressure vessels offer flexibility and savings, both in terms of energy and cost. Compared to liquid hydrogen tanks, insulated pressure vessels save over 20% of the energy consumption, due to the reduced evaporative losses and the reduced need to liquefy hydrogen. Compared to compressed hydrogen storage, insulated pressure vessels offer a 50% cost reduction for the manufacture of the pressure vessel, due to the smaller vessel size required.
Considering all the potential benefits of insulated pressure vessels, it is important to determine what type of pressure vessel could be operated at both high pressure and cryogenic temperature. Of the available pressure vessel technologies commonly used for vehicular storage of natural gas [2] it appears that aluminum-lined, composite-wrapped vessels have the most desirable combination of properties for this application with their low weight and affordable price. However, commercially available aluminum-composite pressure vessels are not designed for low temperature applications.
This paper describes work directed at verifying that insulated pressure vessels can be used safely for vehicular hydrogen storage. The paper describes multiple tests and analyses that have been conducted to evaluate the safety of insulated pressure vessel utilization. Insulated pressure vessels have been subjected to multiple DOT, ISO and SAE certification tests, and the vessels have always been successful in meeting the passing criteria for the different tests. The paper also describes a draft procedure for insulated pressure vessel certification that has recently been generated to assist in a future commercialization of this technology. Ongoing work includes the demonstration of this technology in a vehicle.

2. Pressure Vessel Testing

2.1 Pressure and Temperature Cycling

Pressure vessels have been cycled through 900 high-pressure cycles and 100 low-temperature cycles. The cycles are alternated, running 9 pressure cycles followed by a temperature cycle, and repeating this sequence 100 times. This test is expected to replicate what would happen if these vessels were used in a hydrogen or natural gas-fueled car. Aramid-aluminum and carbon fiber-aluminum pressure vessels have been cycled. The vessels have not failed during the test.

2.2 Burst Test

The aramid-aluminum and the carbon fiber-aluminum pressure vessels were burst-tested after being cycled at cryogenic temperature. The burst test was conducted according to the DOT standards [3]. Failure occurred by hoop mid cylinder separation, which is the preferred mode of failure. The burst pressure was 94.2 MPa, which is substantially higher than the minimum burst pressure of 72.4 MPa.

2.3 Finite Element Analysis

Cyclic and burst testing of the pressure vessels has been complemented with a finite element analysis. The finite element analysis is done to determine whether low temperature operation can result in damage to the pressure vessel. Finite element analysis has been conducted with a commercial finite element package [4]. An axisymmetric mesh was developed consisting of 1195 elements. Physical properties of fiber-epoxy laminate were obtained from available literature at ambient and cryogenic temperatures [5,6].

Finite element analysis of the pressure vessel considers the manufacture of the pressure vessel, starting from the curing process and continuing with the autofrettage cycle. The autofrettage is a process in which the vessel is subjected to a high internal pressure (45.5 MPa, in this case) to introduce a level of plastic deformation and pre-stress. After the autofrettage, the vessel is subjected to a series of low temperature and high-pressure cycles. These are identical to the sequence used for the cyclic test of the pressure vessel, consisting of a cryogenic cycle followed by nine high pressure cycles.
The results of the finite element analysis show that the autofrettage cycle introduces a high level of plastic deformation. After this, the cryogenic cycles also introduce some plastic deformation in the liner. However, successive cryogenic cycles introduce less and less plastic deformation, until the plastic deformation asymptotes to a value slightly higher than 4%. Further cycles do not increase the level of plastic deformation, and therefore the pressure vessel is not expected to fail due to repeated cryogenic cycles. This is in agreement with the cryogenic cyclic tests, in which the vessels were subjected to 100 cryogenic cycles with no damage or failure.

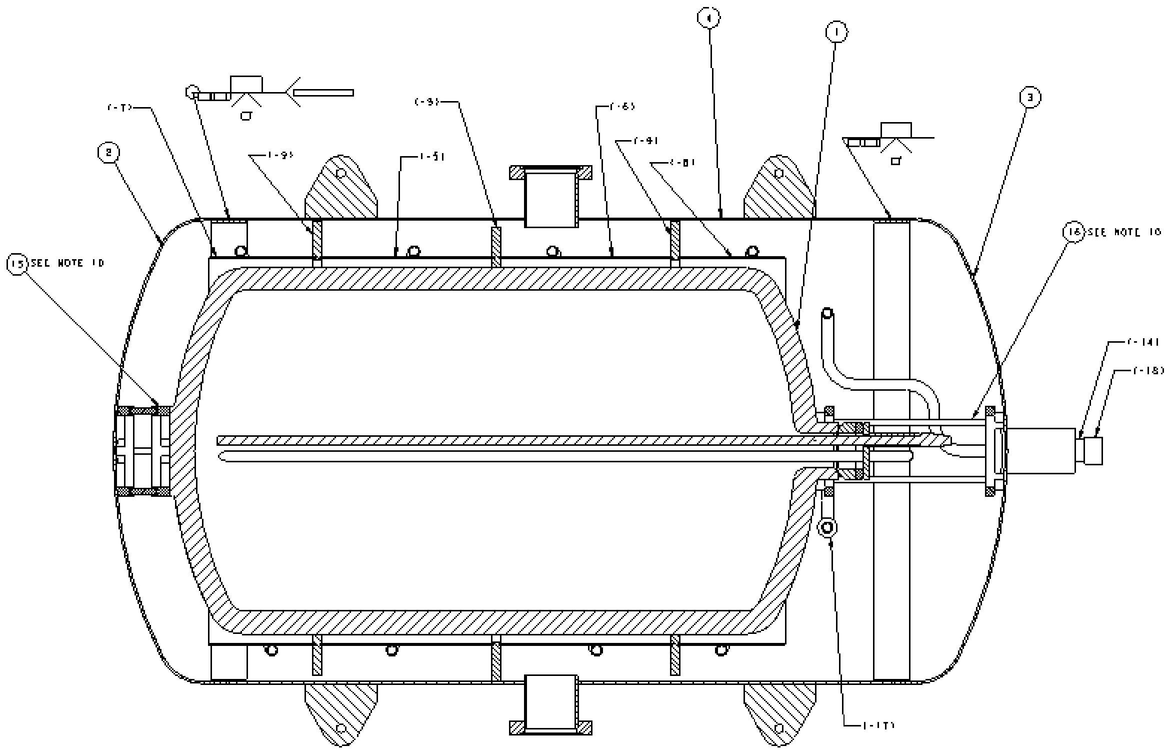

Figure 3. Insulation design for second-generation pressure vessel. The figure shows a vacuum space, for obtaining good performance from the multi-layer insulation, instrumentation for pressure, temperature and level, and a vapor shield for reducing hydrogen evaporative losses.

2.4 Insulation Design and Insulated Pressure Vessel Construction

Insulated pressure vessels have been designed to operate with a multi-layer vacuum superinsulation (MLVSI). MLVSI has a good thermal performance only under a high vacuum, at a pressure lower than 0.01 Pa (7.5×10^{-5} mm Hg [7]). Therefore, the use of MLVSI requires that an outer jacket be built around the vessel. Two designs for the insulation have been built: a first-generation design and a second-generation design. The first-generation vessel is a 1/5-scale vessel that stores about 1 kg of liquid hydrogen. This design was been built for cyclic testing and for DOT certification tests.
The second-generation pressure vessel design is shown in Figure 3. This vessel can store

about 9 kg of liquid hydrogen. This design includes a vapor shield to reduce evaporative losses in addition to instrumentation for pressure, temperature and level, as well as safety devices to avoid failure in case the hydrogen leaks into the vacuum space. Six vessels of the second generation have been built, and have been used for DOT and SAE certification tests, and for incorporation into demonstration vehicles.

2.5 Testing with Liquid and Gaseous Hydrogen

A first-generation insulated pressure vessel has been tested with liquid and gaseous hydrogen. The vessel was first shock-tested and leak-tested. The insulated pressure vessel was then transported to a remote facility for testing with liquid hydrogen. Testing involved filling the vessel with LH_2 to study the insulation performance, the performance of the sensors, and the problems involved with pumping the LH_2 into the vessel. This test is expected to replicate what would happen to the vessel during fueling and operation in an LH_2-fueled car. The test was conducted successfully. There was no damage to the vessel due to the low temperature operation, all the instrumentation operated properly at the low temperature.

2.6 DOT, ISO and SAE Certification Tests

Insulated pressure vessels have been subjected to certification tests according to existing standards [2,8]. A list of the tests that have been performed is shown next. In all tests the insulated pressure vessels successfully met or exceeded the passing criteria.

1) Cycling, ambient temperature. 10000 cycles from less than 10% of the service pressure to the service pressure, 10 cycles per minute maximum [2]. Each test cylinder must withstand the cycling pressurization test without any evidence of visually observable damage, distortion, or leakage.
2) Cycling, environmental. 1) 5000 cycles from zero to service pressure with tank at 60°C and air at ambient temperature and 95% humidity, 2) 5000 cycles from zero to service pressure with tank at –51.1°C and air at ambient temperature, 3) 30 cycles from zero to service pressure, ambient conditions 4) burst test the cycled vessel [2]. Each test cylinder must withstand the cycling pressurization test without any evidence of visually observable damage, distortion, or leakage.
3) Cycling, Thermal. 1) 10 000 cycles from zero to service pressure at ambient temperature, 2) 20 thermal cycles with tank temperature varying from 93.3°C to –51.1°C at service pressure, 3) burst test the cycled vessel [2]. Each test cylinder must withstand the cycling pressurization test without any evidence of visually observable damage, distortion, or leakage.
4) Gunfire. Pressurize vessel with air or nitrogen to service pressure, and impact the vessel with a 0.30 caliber armor-piercing projectile with a speed of 853 m/s. The cylinder is positioned in such a way that the impact point is in the cylinder side wall at a 45° angle with respect to the longitudinal axis of the cylinder. The distance from the firing location to the cylinder may not exceed 45.7 meters [2]. The cylinder shall not fail by fragmentation.
5) Bonfire. Pressurize cylinder with air or nitrogen to service pressure. Set pressure relief devices to discharge at 83% of the cylinder test pressure. The cylinder shall be exposed to fire until the gas is fully vented. The temperature measured on the surface tank exposed to the fire has to be between 850 and 900°C [2]. The venting of the gas must be predominantly through the pressure relief device.
6) Drop Test from 3 m. 1) The cylinder is dropped vertically onto the end, 2) the cylinder is dropped horizontally onto the side wall, 3) the cylinder is dropped onto a 3.8 x 0.48 cm piece of angle iron, 4) after the drops, the vessel is cycled over 1000 pressure cycles from 10% of service pressure to the service pressure, at 10 cycles per minute [2]. The cylinder

is then burst tested; the burst pressure of this vessel has to be at least 90 % of the minimum burst pressure.

7) Cryogenic drop tests from 10 m. The drop test subjects a full-size vehicle fuel tank to a free-fall impact onto an unyielding surface from a height of 10 m. The fuel tank impacts the outer shell on the critical area as determined by the manufacturer. The fuel tank is filled with an equivalent full weight of liquid nitrogen saturated to at least 50% of the maximum allowable working pressure of the fuel tank [8]. There shall be no loss of product for a period of 1 hour after the drop other than relief valve operation and loss of vapor between the filler neck and the secondary relief valve in the case of a test involving the filler neck. Loss of vacuum, denting of the vessel, piping and piping protection, and damage to the support system are acceptable.
8) Flame test with cryogenic fill. The tank should contain an equivalent full level of liquid nitrogen saturated at one half the maximum allowable working pressure (MAWP). The tank should be inverted and subjected to an external temperature of 538^{o}C for 20 minutes without the vessel reaching relief pressure [8].

3. Insulated Pressure Vessel Certification

All tests and analyses conducted to date indicate that insulated pressure vessels can safely be used to store cryogenic and ambient temperature compressed hydrogen or natural gas for vehicular applications. The safety of insulated pressure vessels, along with their advantages for vehicular fuel storage opens the way for future commercialization of this technology. However, commercialization of insulated pressure vessels may still be limited due to the lack of a certification procedure. To address this issue we have developed a list of tests that may be applicable to determine whether an insulated pressure vessel is safe to operate. The list was developed by studying existing pressure vessel standards [2,8], to determine which tests need to be applied to insulated pressure vessels. From these standards we generated a list of 28 ambient temperature tests and 4 cryogenic tests. The list of tests has been documented into a report [9]. This report has been circulated to private industry and regulating organizations for their comments. It is considered that this report can be used as a starting point to generate an official certification procedure to be approved by a regulating agency, such as SAE or ISO.

4. Technology Validation

For a demonstration of the technology we are working on installing an insulated pressure vessel in a Ford Ranger pickup truck powered by a hydrogen internal combustion engine. Integration of insulated pressure vessels into vehicles will include the necessary changes to the vehicle’s fuel system to accommodate either liquefied or compressed hydrogen, as well as the location for fueling connectors, pressure relief devices, vents, etc. The vehicle will then be tested for a period of six months at SunLine Transit (Thousand Palms, California). The drivers and service personnel will thoroughly document fuel use, instrumentation performance, vehicle performance, refuelability issues, etc. Experiences obtained during operation is expected to greatly assist in future commercialization efforts by showing potential design improvements to be implemented in future vessel designs.

5. Conclusions

Insulated pressure vessels are being developed as an alternative technology for storage of hydrogen and natural gas in light-duty vehicles. Insulated pressure vessels can be fueled with cryogenic liquid, cryogenic compressed gas or compressed fuel. This flexibility results in advantages compared to conventional storage technologies. Insulated pressure vessels are lighter than hydrides, more compact than ambient-temperature pressure vessels that store the same mass of fuel, and when compared to conventional cryogenic liquid fuel tanks they have lower evaporative losses and require lower energy input when filled with compressed gas.

For reduced cost and complexity it is desirable to use commercially available aluminum-fiber pressure vessels as components for the insulated pressure vessels. However, commercially available pressure vessels are not designed for operation at cryogenic temperature. A series of tests has been carried out to verify that commercially available pressure vessels can be operated at cryogenic temperature with no performance losses. All analyses and experiments to date indicate that no significant damage has occurred. Ongoing activities include a demonstration project in which the insulated pressure vessels is being installed in a vehicle.

6. Acknowledgments

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